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Removal of ammoniacal nitrogen from Malaysian palm oil mill effluent (POME) using optimized operating parameters of peat soil as natural adsorbent

Md. Arif Hossen [a,b], Nurashikin Yaacof [a,*], Fariha Najwa Azahar [a], Noraziah Ahmad [a], Azrina Abd Aziz [a,c]

[a] Faculty of Civil Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, Gambang, Pahang 26300, Malaysia
[b] Institute of River, Harbor and Environmental Science (IRHES), Chittagong University of Engineering & Technology, Chattogram 4349, Bangladesh
[c] Advanced Intelligent Materials Centre, Universiti Malaysia Pahang Al-Sultan Abdullah, Gambang, Pahang 26300, Malaysia

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ABSTRACT

Nowadays, the use of natural absorbents to remove pollutants from POME has gained remarkable attention. The main objective of this study is to investigate the suitability and performance of modified peat soil as an adsorbent for the removal of NH_3-N from POME. The chemical activation method was performed using readily available NaOH for the first time to improve the adsorption performance of naturally available low-cost peat soil. The physical properties of raw and modified peat soil were determined using water-holding capacity, moisture content, bulk density, porosity, and BET surface area. The adsorbents were also characterized by SEM and FTIR to investigate surface morphology and chemical composition. To optimize the experimental parameters namely adsorbent dosage, agitation rate, and contact time for removal of NH_3-N from POME, response surface methodology (RSM) was employed in this study with two different activation ratios. Substantial improvement of physical properties was attained after the modification of raw peat soil. The SEM images of modified peat soil showed a more porous space structure with larger voids while the FT-IR demonstrated the distinctive functional groups in the raw and modified peat soil. At optimized conditions of 5.71 g/L adsorbent dosage, 50 rpm agitation rate, and 38.96 min contact time predicted removal efficiency of NH_3-N has been revealed 64.06 and 58.74 % at 1:20 and 1:30 activation ratios, respectively. The experimental investigation using optimized parameters showed 69.12 ± 2.5 and 61.57 ± 4.3 % removal of NH_3-N. The experimental and predicted results showed good agreement. The rapid removal of NH_3-N (69.1 % within 39 min) was achieved by chemically modified peat soil in this study compared to previously reported studies. Nevertheless, the raw and modified peat soil showed good stability up to three cycles of reusability.

1. Introduction

The palm oil industry is one of the most economic contributors for countries like Malaysia and Indonesia. In 2020, 72.04 million tons of palm oil were produced globally, with Malaysia producing 19.14 million tons of that total (Mahmod et al., 2022). According to estimates, 5–7.5 tons of water are needed for producing one ton of crude palm oil, with half of that amount being released as palm oil mill effluent (POME) (Ahmad et al., 2003). The residual water is either treated or left untreated before being released into nearby water bodies (Liew et al., 2015; Ahmad et al., 2022). It has been reported by Cheng et al. (2021), the effluent from the processing of palm oil generates a very foul scent that makes the surrounding areas uncomfortable. Odour commonly exists as a form of gas such as ammonia (NH_3), which is produced by anaerobic bacteria via anaerobic digestion. NH_3 gas is a troublesome gas with a strong and suffocating smell (Lemes et al., 2023). Regarding NH_3, its acute burning of the eyes, nose, throat, and respiratory system can induce blindness and damage to the lungs due to the high exposure levels found in the air (Yujing et al., 2022). According to Yaacof et al. (2019), it is possible to smell palm oil mill effluent (POME) up to 1.5 km away from the mill, and occasionally even up to 5 km distant. As the industry continues to grow, these issues may only intensify. Therefore,

* Corresponding author.
E-mail address: nurashikin@umpsa.edu.my (N. Yaacof).

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NH_3 concentrations have to be reduced for odour management and to minimize potential health risks.

There are various methods to remove ammoniacal nitrogen (NH_3-N) from wastewater (Sheikh et al., 2023). Use of adsorbents is one of the effective technologies from practical point of view and affordability. For example, Adeleke et al. (2017) employed activated cow bone powder adsorbent for removal of NH_3-N and chemical oxygen demand (COD) from POME. Manikam and coworkers (2019) utilized palm oil fuel ash (POFA) as adsorbent to remove NH_3-N and nitrate from sewage wastewater. Natural zeolite activated by heat was utilized as adsorbents by Aziz et al. (2020) to remove colour, COD and NH_3-N from landfill leachate. Fe-functionalized crab shells have been applied to absorb NH_3-N from slaughterhouse wastewater (Ohale et al., 2022).

Peat soils have the ability to become an adsorbent media since it contains high carbon content and a high density of porosity (Budihardjo et al., 2021). The other properties of peat soil that can make peat soil as efficient adsorbent are its high content of lignin, cellulose, and minerals such as magnesium (Mg), iron (Fe), and silicon (Si) where those minerals linked to the surface of acid functional groups (carboxyl -COOH, phenolic -OH, sulphonic -SO_3H), which enable the exchange of H^+ ions for other cations (Singh et al., 2020). There are two methods usually used to modify adsorbent performance namely, chemical and physical modification (Bello et al., 2017; Abegunde et al., 2020). For instance, Mohamad et al. (2018) prepared composite adsorbent by mixing peat soil, laterite soil and rice husk for the removal of heavy metals from municipal landfill leachate. The physical and chemical characteristics of the hybrid adsorbent mixture were enhanced by the varying percentage ratios of rice husk to peat soil, which in turn had a significant impact on the removal efficiency of heavy metals. Budihardjo and coworkers (2021) also modified peat soil following the physical modification approach. They utilized activated carbon and coal to modify raw peat soil for the application of heavy metal removal from simulated landfill leachate. The improved surface area of the modified peat soil facilitated heavy metal adsorption utilizing the adsorbent's pores. Detho and his group (2022) employed coconut shell activated carbon to modify peat soil for the removal of COD and NH_3-N from municipal leachate. The physicochemical properties of the modified adsorbents improved considerably at 2.0:2.0 g activation ratio, which resulted 76 % and 65 % removal of COD and NH_3-N, respectively. Despite being cost-effective, the efficiency of physically modified adsorbents is still low. The chemical modification approach has not been yet implemented for improving the adsorption performance of peat soil.

In this study, the raw peat soil was activated by using the chemical activation process since the chemical process is reported as efficient compared to the physical process (Abegunde et al., 2020). Norouzi et al., (2018) applied NaOH to chemically modify activated carbon and demonstrated enhanced Cr(VI) adsorption performance. The KOH-activated porous biochar exhibited superior adsorption performance to remove Cr(VI) from wastewater (Qu et al., 2021). The NaOH was used in this study as a chemical agent to activate raw peat soil as NaOH is readily available from industry. Compared to KOH, NaOH activation has advantages such as lower dosage, lower cost, and greater environmental friendliness (Beltrame et al., 2018; Bergna et al., 2020).

The purpose of the study is to investigate the suitability and performance of modified peat soil as an absorbent for the removal of NH_3-N from POME. Peat soil was chosen because it is cost effective and widely available in Malaysia. This study also includes an experimental design via response surface methodology (RSM) in which to examine the effects of three independent variables namely adsorbent dose, agitation, and contact time on the removal of NH_3-N from the POME sample. This study may serve as a benchmark for future research on low-cost adsorbents for eliminating malodor from POME and other effluents.

2. Materials and methods

2.1. POME sampling

The POME sample was collected twice per month from the first anaerobic pond of a palm oil mill situated at Felda Lepar Hilir 3, Gambang, Malaysia (102°59'15" E, 3°39'37" N) using polypropylene bottles. Before collection, the bottles were thoroughly cleaned and rinsed with effluent to prevent contamination and dilution. The samples were taken back to the lab after collection and kept there in a chiller at 6°C to preserve their original state for further examination and analysis. Within 24 hours following sample collection, the analysis of several parameters was conducted.

2.2. Adsorbent preparation

The adsorbents were prepared by chemical activation with sodium hydroxide (NaOH) solution. The experimental procedure for the preparation of absorbent and removal of NH_3-N from POME is presented in Fig. 1. At first, peat soil was extracted at a depth of 5–20 cm adjacent to Jalan Gambang, Malaysia. Peat soil was dried at 110°C (ASTM, D2974) in oven for 24 hours to remove all pore water from the soil. After drying, peat soil was sieved by a sieve of 1 mm mesh size. The particle size is obtained by using standard mesh sieves (standard sieve AS 200) to obtain particles of sizes up to 0.375 and 1.0 mm (ASTM, D2974). The ratio between raw peat soil (g) and NaOH solutions (mL) was taken 1:20 and 1:30 after applying several other ratios as trial. Different percentages of NaOH were applied to improve the physical properties of peat soil. Initially, 10 mL of 2 M NaOH solution and 990 mL of deionized water were added in a beaker. Then, 10 g of peat soils were impregnated with 200 mL of dilute NaOH solution for preparation of 1:20 solution. The test solutions were stirred with magnetic stirrer on a hot plate at 85°C for 8 hours. After cooling, the sample was subjected to thorough washing with distilled water until the samples obtained by filtration showed neutral pH which was 6.5–7.5 value by pH meter to ensure total remove of acid. Then, the samples were dried in oven at 120°C for 5 hours before the experiment. The step was repeated for ratio 1:30 NaOH activation.

2.3. Adsorbent materials characterization

To evaluate the physical properties of adsorbent materials, water holding capacity (%), moisture content (%), bulk density (g/mL), and porosity (%) were determined before and after chemical treatment. The water holding capacity was determined using Eq. (1). Prior to pouring the peat soil, the container has been weighed. After adding the peat soil, the container was measured and heated to 105°C for 24 hours. After 24 hours, the sample was weighed (W_d) and the data was recorded. The same material was then weighted (W_w) again after being soaked in water for 48 hours.

$$\text{Water holding capacity} = \frac{(W_w - W_d)}{W_d} \times 100\% \quad (1)$$

To determine the mass of water present in a sample of peat soil at ambient temperature, the moisture content was calculated by following Eq. (2). Where, W_i is the initial weight before dried in oven at 105° C for 3 h and W_f refers to the final weight after drying.

$$\text{Moisture content} = \frac{(W_i - W_f)}{W_i} \times 100\% \quad (2)$$

Bulk density of the samples was measured with Eq. (3). Porosity is usually expressed as a percentage of the total volume of material. To determine the porosity of adsorbent, peat soils were filled in a container and the total volume (V_t) of the container has been measured. A measuring cylinder was used to measure 1000 mL of water, and the water was then poured into the container holding the sample (500 mL of

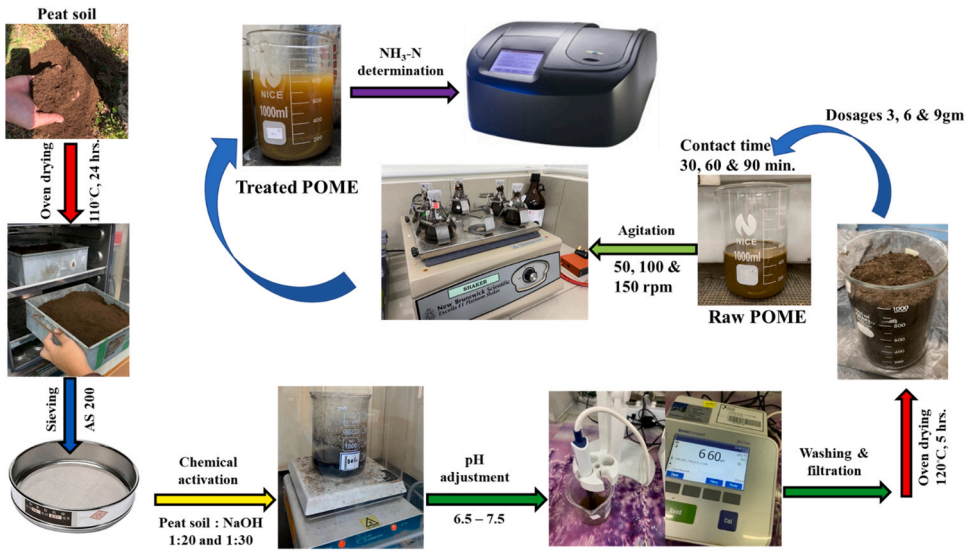

Fig. 1. Experimental procedure to prepare natural adsorbent and organic pollutants removal.

sample), filling it to the top. Subtracts the volume of water that was still inside the cylinder from the overall amount of water. The difference in volume of the container and the volume of water filled was recorded as V_v. Finally, the porosity of the peat soil before and after chemical activation was determined through Eq. (4). Tests were carried out three times to determine the average value for the quantification of each physical property.

$$\text{Bulk density}\left(\text{g}\Big/\text{mL}\right) = \frac{\textit{Mass of sample}}{\textit{Volume of container}} \tag{3}$$

$$\text{Porosity} = \frac{V_v}{V_t} \times 100\% \tag{4}$$

The samples of adsorbents were also examined by a Scanning Electron Microscope (SEM) and Fourier-Transform Infrared (FTIR) for surface morphology and chemical composition. The oven dried peat samples used in this test were coated with gold before taking SEM (JEOL, JSM-IT200) images. The chemical characterization of the functional groups of peat soil was analyzed by a Thermo Fisher Scientific Nicolet iS50 FTIR. The analysis was carried out at room temperature by using Potassium Bromide (KBr) pellet technique where the absorbance spectrums were recorded in the range 440–3900 cm^{-1} with a resolution of factor 4 cm^{-1}. The specific surface area of raw and modified peat soils was analyzed by BET N_2 adsorption desorption method (Micrometrics, ASAP2020).

2.4. Adsorption experiments

In each adsorption experiment, 1000 mL of POME was added to different amounts of adsorbent (3, 6 and 9 gm) in a conical flask covered by aluminum foil as a lid to prevent contamination of microorganisms from surrounding air. The samples were then agitated at 50, 100 and 150 rpm with time variations of 30–90 min. The concentration of NH_3-N in raw and treated POME was determined using calibrated spectrophotometer (Hatch DR5000). The removal efficiency was calculated by using the following Eq. (5).

$$\text{Removal Efficiency}(\%) = \frac{C_i - C_f}{C_i} \times 100 \tag{5}$$

Where, C_i and C_f are the concentrations of NH_3-N (mg/L) in raw and treated POME.

2.5. POME analysis

According to the accepted procedures outlined by the American Public Health Association, the physicochemical parameters of the collected POME samples, including pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solid (SS), and ammoniacal nitrogen (NH_3-N), were measured (APHA, 2005).

2.6. Experimental optimization

Response surface methodology (RSM) was utilized to examine the effects of three independent variables namely adsorbent dosage (X_1), agitation (X_2) and contact time (X_3) on removal of NH_3-N (Y). RSM is a popular statistical and mathematical tool employed to optimize operating parameters by serving as an experimental design. The variables were generated and examined using the Design Expert software (version SE360). Design-Expert is an intuitive software that provides robust parameters design with reliable screening, characterization, optimization, and comparison testing (Rampado and Peer, 2023). The number of experiments (20) that would be examined for the optimization of the variables and responses was chosen using the central composite design (CCD) method. The ranges of input parameters have been chosen from the available literature related to the removal of NH_3-N using adsorbents (Adeleke et al., 2017; Detho et al., 2022; Ohale et al., 2022). The actual and coded levels of variables are listed in Table 1. The relationship between the actual variables (φ_i) and coded variables (x_i) can be expressed by Eq. (6).

$$x_i = \frac{\varphi_i - \frac{(H_L + L_L)}{2}}{\frac{(H_L - L_L)}{2}} \tag{6}$$

Table 1
Control variables and their respective levels.

Control variables	Coded symbols	Levels				
		-α	Low (-1)	Mid (0)	High (1)	+α
Adsorbent dosage (g/L)	X_1	0.95	3	6	9	11.05
Agitation rate (rpm)	X_2	15.91	50	100	150	184.09
Contact time (min.)	X_3	9.55	30	60	90	110.45

Where H_L denotes the independent variable's highest value and L_L denotes its lowest value.

The second-order polynomial equation was established for the removal of NH_3-N as following:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{k}\beta_{ii}X_i^2 + \sum_{i=1}^{k}\sum_{j<1}^{k}\beta_{ij}X_iX_j \quad (7)$$

In the above equation, Y is the predicted response for the removal of NH_3-N, and β_0, β_i, β_{ii}, β_{ij} are the regression coefficients. X_i and X_j represent independent variables in coded form, while k is the number of independent variables. The independent variables and dependent variables are summarized in Table 2. Using the analysis of variance, the impact of factors on the adsorption process was examined (ANOVA, $p < 0.05$).

3. Results and discussion

3.1. Characteristics of POME

The raw POME samples used in this study were analyzed for determining physicochemical parameters and presented in Table 3. Normally, in the literature the pH of conventional POME water was reported in the range of 3.4–5.2, in the present study it was also found 4.2 ± 0.46, which is below the standard of industrial effluent discharge quality in Malaysia (5.5–9.0). In the current investigation, the raw POME has significant concentrations of BOD (56839 ± 120 mg/L), COD (84927 ± 218 mg/L), and SS (27963 ± 108 mg/L), which is the indicator of the high levels of organic matter. The findings are in line with the earlier studies that have been published (Iskandar et al., 2018; Mahmod et al., 2022). The concentration of ammoniacal nitrogen (NH_3-N) was found at an elevated level 87 ± 5.2 mg/L compared to previous studies and standards (Sa'at et al., 2019).

3.2. Characteristics of adsorbent

The physical properties of peat soil utilized in this study are presented in Table 4. Substantial improvement was attained after the modification of peat soil by chemical activation approach. The water holding capacity and moisture content of any adsorbent are very important to adsorb pollutants (Yang et al., 2021). The other crucial properties of adsorbents are porosity and specific surface area which significantly influence the pollutants' adsorption (Qu et al., 2021; Gupta et al., 2022). Compared to 1:30 NaOH activated modified peat soil, the adsorption properties of 1:20 NaOH was improved considerably. This may be due to the overdosing of NaOH during chemical activation (Aziz et al., 2020). The porosity of 1:20 NaOH activated peat soil improved from 70 % to 76 % after modification. As the porosity improved, the BET surface area of 1:20 NaOH modified peat soil increased from 1.85 g/m^2 to 5.49 g/m^2. For 1:30 NaOH modified peat soil the water-holding capacity improved by around 30 % compared to raw peat soil, while moisture content was also reduced 15 % as porosity decreased. Even though porosity of 1:30 NaOH decreased, the BET surface area increased (2.07 g/m^2) slightly compared to raw peat soil.

To examine the surface morphology and chemical composition of the adsorbent materials SEM and FT-IR were performed. Fig. 2 presents the SEM images before and after chemical activation. From Fig. 2, it is possible to observe how the adsorbent's various textural characteristics have changed before and after treatment. Fig. 2**a** makes it abundantly evident that raw peat soil has less fiber and organic content than the treated sample, and it is also less flaky and granular. Given the presence of flaky structures in the SEM image, the peat exhibits poor shear strength along with substantial compressibility (Paul and Hussain, 2020). In contrast to raw peat soil, the modified peat soils exhibited more fibrous and organic content with a more porous space structure (Fig. 2**b, c**). The presence of highly perforated particles in peat makes it more compressible and permeable in nature (Paul et al., 2021). It is apparent that activation results in considerable alterations to the size and number of pores. The FT-IR of raw and treated peat was investigated within the wavenumber of 1000–3500 cm^{-1} as the major peaks of peat soil existed within that range. As shown in Fig. 3, there are three distinct peaks between 1000 and 1700 cm^{-1} is detected at 1080.24, 1381.05, and 1635.64 cm^{-1} which represent the stretching vibrations of C–O, C–C, and C=O, respectively (Adeleke et al., 2017; Ouachtak et al., 2023). The stretching vibration of O=C=O and C-H can be seen as two tiny peaks at 2368.63 cm^{-1} and 2924.34 cm^{-1} (Budihardjo et al., 2021). At 3488.72 cm^{-1}, a wide adsorption peak identifies the hydroxyl (O-H) groups (Lanan et al., 2021). As seen in Fig. 3 for treated peat soil, there are substantial variations at the peaks of functional groups particularly near at 3500 cm^{-1} since the interaction with NaOH altering the molecule's internal structure.

Table 2
Central composite design parameters and results for the response variables adsorption rate at 1:20 and 1:30 NaOH activation.

Run No.	Experimental variables			Response variables	
	Adsorbent dosage (X_1)	Agitation rate (X_2)	Contact time (X_3)	Adsorption rate (%) for 1:20 NaOH activation	Adsorption rate (%) for 1:30 NaOH activation
01	11.05	100	60	55	55
02	9	50	90	52	79
03	9	50	30	57	76
04	0.95	100	60	31	33
05	6	100	60	79	57
06	6	15.91	60	63	61
07	6	100	60	78	58
08	9	150	30	52	40
09	3	150	30	38	52
10	6	100	9.55	48	47
11	6	100	60	79	57
12	3	50	30	36	48
13	9	150	90	44	40
14	6	184.09	60	59	36
15	6	100	110.45	69	52
16	6	100	60	80	56
17	6	100	60	79	57
18	3	50	90	53	53
19	6	100	60	81	58
20	3	150	90	51	42

Table 3
Physicochemical characteristics of POME.

Parameters	Mean	Range[a]	Standards[b]
pH	4.2 ± 0.46	3.4–5.2	5.5 – 9.0
BOD	56839 ± 120	10,250–43,750	50
COD	84927 ± 218	15,000–100,000	200
Suspended solids	27963 ± 108	5000–54,000	100
Ammoniacal nitrogen	87 ± 5.2	4–80	20

Note: All parameter units are in mg/L except pH.
[a] Range of POME quality taken from Iskandar et al. (2018).
[b] Environmental Quality (Industrial Effluents) Regulations 2009. Department of Environment, Malaysia (DOE, 2009).

Table 4
Physical characteristics of peat and modified peat soils.

Parameters	Raw peat soil	Modified peat soil	
		1:20 NaOH	1:30 NaOH
Water holding capacity (%)	65	62	83
Moisture content (%)	57	51	49
Bulk density (g/mL)	0.31	0.27	0.46
Porosity (%)	70	76	64
BET surface area (m^2/g)	1.85	5.49	2.07

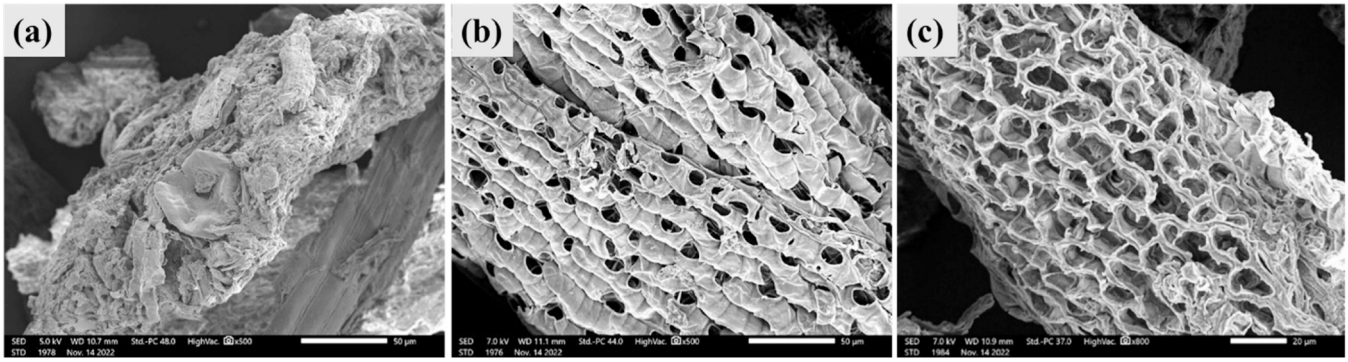

Fig. 2. SEM images of (a) peat soil before activation, (b) 1:20 NaOH activation and (c) 1:30 NaOH activation.

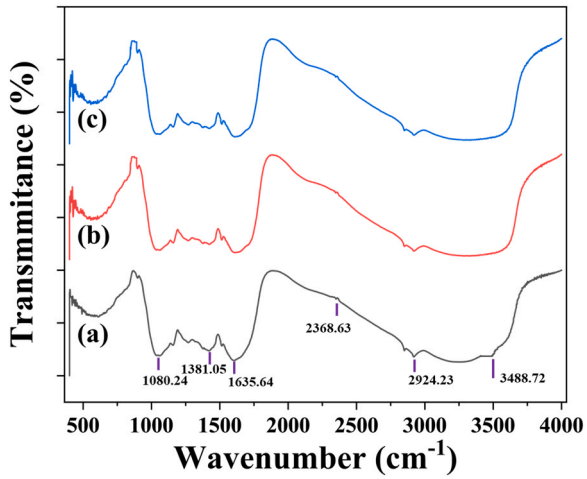

Fig. 3. FTIR spectrum of (a) peat soil before activation, (b) 1:20 NaOH activation and (c) 1:30 NaOH activation.

3.3. Screening of independent variables

To obtain the optimum parameters for NH_3-N removal from POME by a natural adsorbent (peat soil) a central composite design (CCD) with three experimental variables such as adsorbent dosage (X_1), agitation (X_2) and contact time (X_3) was utilized. By adopting chemical activation with a 1:20 and 1:30 ratio of NaOH, the adsorbents were prepared. The responses were examined for both activation ratios. Analysis of variance (ANOVA), one of the recognized approaches, was employed to verify the accuracy of the fitted model. ANOVA suggested the quadratic model for fitting the experimental data. Table 5 displays the ANOVA findings for the reduction of NH_3-N at various NaOH activation ratios. The p-value, F-value, and correlation between the experimental factors and the provided responses were used to assess the statistical significance. A lower P value (<0.0001 for a 1:20 ratio and 0.0001 for a 1:30 ratio) and a larger F value (16.74 for a 1:20 ratio and 11.86 for a 1:30 ratio) supported the significance of the model (Lanan et al., 2021; Wakejo et al., 2022). The study showed that the value of adjusted R^2 (adj. R^2) and predicted R^2 (pred. R^2) were close to each other implying good predictability and comparability of the experimental results with theoretical values. Additionally, a non-significant lack of fit provides an indication that models are sufficiently fit to the experiment data (Fereidonian Dashti et al., 2021; Hossen et al., 2024).

The association between the data set of actual and predicted variables is performed using regression analysis. The best model for fitting the experimental data was a second-order polynomial regression model for NH_3-N removal at a 1:20 activation ratio, while a two-factor interaction model was recommended for NH_3-N removal at a 1:30 activation ratio. The relationship between the input variables for the responses in terms of coded factors is given by Eqs. (8) and (9). Table 6 shows the regression coefficients for reducing NH_3-N in the POME following the adsorption method. Both models were examined using diagnostic plots to further evaluate the prediction competency of a particular model (Fereidonian Dashti et al., 2021). As shown in Fig. 4, both models' predictions for the removal of NH_3-N give results that are acceptable given their R^2 values are more than 0.75. R^2 values of greater than 0.75 are regarded as satisfactory to ensure the model's applicability in forecasting the experimental runs (Lanan et al., 2021).

$$NH_3\text{-N Removal (\%) at 1:20 NaOH activation} = +77.83 + 4.93 * X_1 - 1.44 * X_2 + 3.95 * X_3 - 1.63 * X_1X_2 - 5.38 * X_1X_3 - 0.8750 * X_2X_3 - 13.32 * X_1^2 - 6.96 * X_2^2 - 7.66 * X_3^2 \quad (8)$$

$$NH_3\text{-N Removal (\%) at 1:30 NaOH activation} = +52.85 + 5.64 * X_1 - 9.08 * X_2 + 0.4693 * X_3 - 8.50 * X_1X_2 + 1.00 * X_1X_3 - 2.25 * X_2X_3 \quad (9)$$

To investigate the impact of three independent factors namely adsorbent dosage, agitation rate, and contact time on the effectiveness of removing NH_3–N, surface plots were developed. The combined effects of two independent variables were observed on NH_3-N removal performance keeping the third variables constant. A significant ($P < 0.01$) interaction was found between adsorbent dosage and contact time which substantially improved the reduction of NH_3-N at a 1:20 activation ratio by 78.48 % (Fig. 5**a**). The removal of NH_3-N gradually

Table 5
Analysis of the variance (ANOVA) of the response surface quadratic model for the removal of NH_3-N from POME at different NaOH activation ratios.

Source	Sum of squares		DoF		Mean square		F-value		P-value	
	1:20	1:30	1:20	1:30	1:20	1:30	1:20	1:30	1:20	1:30
Model	4350.98	2190.34	9	6	483.44	365.06	16.74	11.86	< 0.0001	0.0001
Residual	288.77	400.21	10	13	28.88	30.79				
Lack of Fit	193.44	397.38	5	8	38.69	49.67	2.03	87.66	0.2280	0.0801
Pure Error	95.33	2.83	5	5	19.07	0.5667				
Cor Total	4639.75	2590.55	19	19						

Note: $P < 0.01$ highly significant; $0.01 < P < 0.05$ significant; $P > 0.05$ not significant.
Adj. $R^2 = 0.8817$, pred. $R^2 = 0.7545$ (1:20 activation); Adj. $R^2 = 0.7942$, pred. $R^2 = 0.7104$ (1:30 activation).

Table 6
Regression coefficient and their significance of the quadratic and two-factor interaction model for the reduction of NH_3-N from POME at different NaOH activation ratios.

Factor	Coefficients		Standard error		F value		P-value	
	1:20	1:30	1:20	1:30	1:20	1:30	1:20	1:30
Intercept (β_0)	+77.83	+52.85	2.19	1.24	11.51	11.86	< 0.0001	0.0001
X_1 (β_1)	+4.93	+5.64	1.45	1.50	0.9868	14.10	0.0069	0.0024
X_2 (β_2)	−1.44	−9.08	1.45	1.50	7.39	36.60	0.3440	< 0.0001
X_3 (β_3)	+3.95	+0.4693	1.45	1.50	0.7315	0.0977	0.0216	0.7596
X_1X_2 (β_{12})	−1.63	−8.50	1.90	1.96	8.00	18.78	0.4124	0.0008
X_1X_3 (β13)	−5.38	+1.00	1.90	1.96	0.2121	0.2599	0.0019	0.6188
X_2X_3 (β_{23})	−0.8750	−2.25	1.90	1.96	88.55	1.32	0.6550	0.2721
X_1^2 (β_{11})	−13.32		1.42		24.15		< 0.0001	
X_2^2 (β_{22})	−6.96		1.42		29.31		0.0006	
X_3^2 (β_{33})	−7.66		1.42		11.51		0.0003	

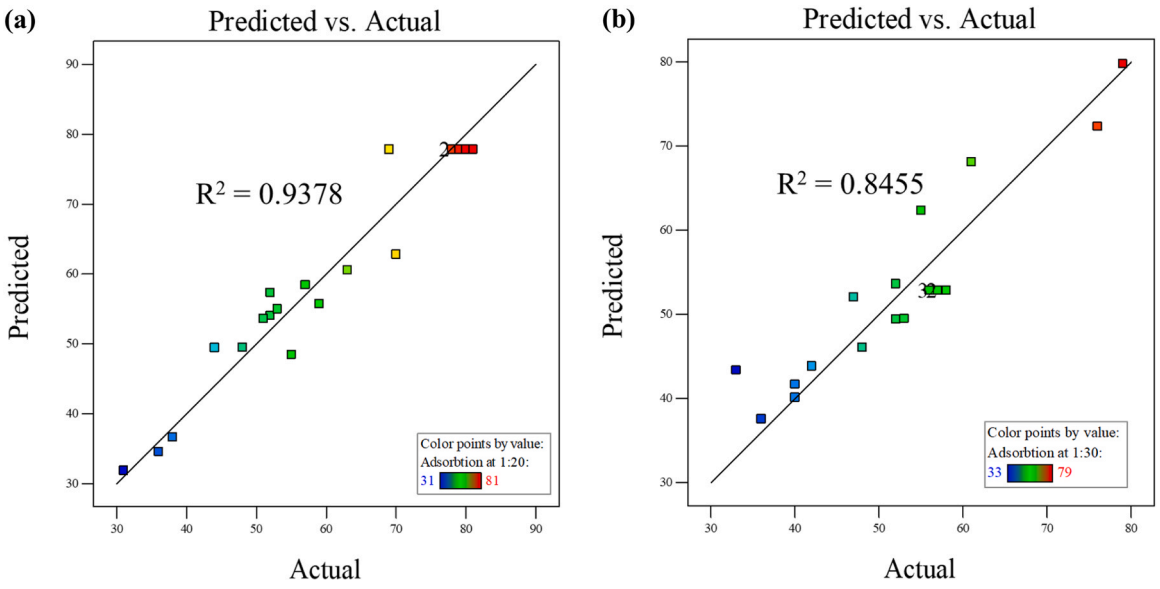

Fig. 4. Correlation between predicted and actual values of response for (a) 1:20 activation and (b) 1:30 activation.

increased as the adsorbent dosage increased from 3 g/L up to an approximate 5.71 g/L and consequently showed decreasing trend until adsorbent dosage reached 9 g/L. The availability of the adsorption sites improves the adsorption capacity to an optimum level, which may be explained by the development in the number of active adsorption sites (Ismail et al., 2022; Raji et al., 2023). However, when the adsorption capacity reaches the maximum level, it starts to decrease even further increase in adsorbent dosage (Battas et al., 2019; Mehmood et al., 2022). Similarly increasing and decreasing trends were also noticed for the removal of NH_3-N with contact time of 30–90 minutes and reached the optimum level at a contact time of around 40 minutes. Excellent adsorption kinetics of the prepared adsorbent was evident since the good adsorption capacity was reached with the least amount of contact time (Wakejo et al., 2022; Sireesha et al., 2023). For activation ratio 1:30, significant interaction was observed between adsorbent dose and agitation rate. The increasing trend was revealed with the higher adsorbent dosages and lower agitation rate (Fig. 5**b**). A similar adsorption trend was observed by Wakejo et al. (2022) in the adsorption of Ciprofloxacin from water using chemically modified biochar. The optimum NH_3-N removal has been found to be 58.3 % at 6 g/L adsorbent dosage and 90 rpm.

3.4. Optimized experimental conditions

The optimal experimental parameters of the adsorption process for the removal of NH_3-N were perceived at an adsorbent dosage of 5.71 g/L, an agitation rate of 50 rpm, and 38.96 min contact time. In this study, the optimal removal efficiency of ammoniacal nitrogen from POME was achieved by choosing the minimal adsorbent dose, agitation rate, and contact time. The optimized outcomes had a desirability of 0.81, demonstrating the applicability of the proposed models. The most preferable value for desirability corresponds to the number that is closest to 1 (Lee et al., 2018; Kumari and Gupta, 2019). At optimized conditions, 64.06 % and 58.74 % NH_3-N removal were predicted by the model at 1:20 and 1:30 activation ratios, respectively. In order to verify the predicted removal efficiency, further experimental evaluations have been performed. Table 7 presents the predicted and experimental responses at optimized conditions. Referring to Table 7, the observed and predicted reduction of NH_3-N were 69.06 vs. 64.06 % at 1:20 activation ratio and 61.57 vs. 58.74 % at 1:30 activation ratio, respectively. As studied by Adeleke et al. (2017), 75.61 vs. 74.04 % experimental and predicted was found for NH_3-N removal using cow bone powder as an adsorbent. In another study, Daud et al. (2018) examined the performance of a composite adsorbent prepared by mixing moringa leaf powder and zeolite. At optimized conditions, the actual versus predicted reduction was revealed 70.14 against 69.13 % for removal of NH_3-N from landfill leachate.

3.5. Reusability of the adsorbent on NH_3-N removal

The reusability of any adsorbent is the crucial feature for its practical applications in addition to potential adsorption ability (Baskar et al.,

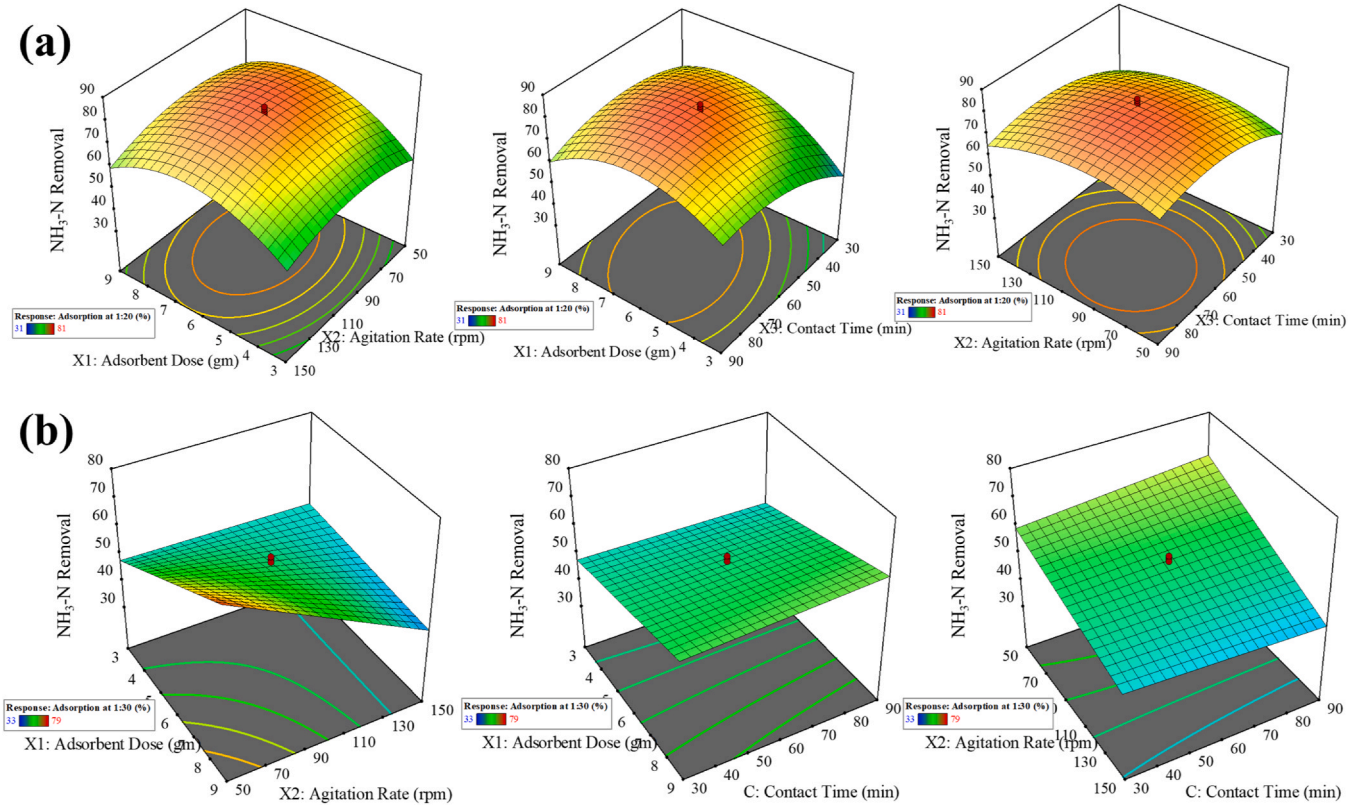

Fig. 5. 3D surface plot showing the interactions between the variables (a) 1:20 NaOH activation and (b) 1:30 NaOH activation.

Table 7
Predicted and experimental response at optimized conditions.

Optimum conditions	Coded levels	Actual levels	% difference	Desirability
Adsorbent dose (gm)	- 1.00	5.71		
Agitation rate (rpm)	- 0.08	50.00		0.81
Contact time (min.)	- 0.85	38.96		
Response	**Predicted**	**Experimental**		
NH_3-N Removal (%) at 1:20 NaOH activation	64.06	69.12 ± 2.5	7.89 %	
NH_3-N Removal (%) at 1:30 NaOH activation	58.74	61.57 ± 4.3	4.81 %	

2022). The performance of raw and modified peat soils to remove NH_3-N from POME is presented in Fig. 6. The average ammoniacal nitrogen removal rate of fresh adsorbents was observed 53.2 %, 69.1 % and 61.6 % for raw, 1:20 NaOH and 1:30 NaOH activated peat soils, respectively. The performance of raw peat soil up to three cycles reuse showed good stability. In contrast to raw peat soil, the NH_3-N removal rates decreased considerably as the number of reuse cycles increased for modified peat soils. The NH_3-N removal rate of 1:20 NaOH activated modified soil after three cycles of reuse observed 58.9 %, which is 10.2 % less compared to initially used sample. The used adsorbents were recycled by simply washing them in water free of ammonia to get rid of any surface contaminants and dried before employing them again. Due

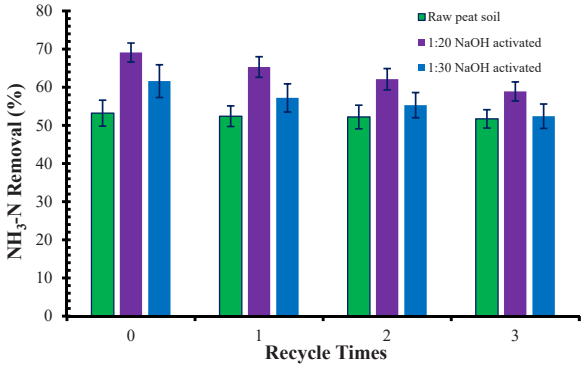

Fig. 6. Stability of raw and modified peat soil for NH_3-N removal from POME.

to the washing of chemically modified peat soils, they might lose their as-formed porous structure, hence reduced their performance. This is consistent with the reusability performance of adsorbent prepared from plant biomass carbon modified by chemical oxidant to remove NH_4^+-N from pickle wastewater (Liu et al., 2023).

3.6. Adsorption performance comparison of peat soil with other adsorbents

To remove ammoniacal nitrogen from contaminated water, a variety of adsorbents have been used extensively in recent times. For efficient removal of NH_3-N from wastewater different experimental parameters including pH, adsorbent dosages, contact time and agitation rate play crucial roles. Table 8 summarizes the recently conducted studies on removal of NH_3-N from wastewater utilizing different adsorbents. The maximum NH_3-N removal efficiency of 92.6 % within 156 min was reported by the utilization of Fe-functionalized crab shells adsorbent

Table 8
Performance comparison of recently used various adsorbents to remove NH_3-N from wastewater.

Adsorbents	Type of wastewater	Optimized parameters				Removal efficiency	Reference
		pH	Dosage	Contact time	Agitation rate		
Coconut shell activated carbon modified peat soil	Municipal solid waste (MSW) landfill leachate	7.0	2 g/L	120 min	200 rpm	70 %	Detho et al. (2022)
Natural zeolite	Sanitary landfill leachate	8.0	133 g/L	120 min	1.18 m/s	72 %	Genethliou et al. (2021)
Heat activated zeolite	Municipal solid waste (MSW) landfill leachate	7.0	25 g/L	90 min	350 rpm	55.8 %	Aziz et al. (2020)
Natural zeolite	Rubber processing industry effluents	7.0	4 g/L	120 min	150 rpm	69 %	Detho et al. (2023)
Fe-functionalized crab shells	Slaughterhouse wastewater	6.5	2.2 g/L	156 min	180 rpm	92.6 %	Ohale et al. (2022)
Green mussel modified zeolite	Municipal solid waste (MSW) landfill leachate	7.0	2 g/L	120 min	200 rpm	65 %	Daud et al. (2022)
Activated carbon and green mussel modified zeolite	Municipal solid waste (MSW) landfill leachate	7.0	1.5 g/L	120 min	200 rpm	67 %	Detho et al. (2021)
Alkali-modified fly ash	Polluted river water	7.0	5 g/L	120 min	350 rpm	80.2 %	Meng et al. (2020)
Modified biochar	Simulated wastewater	7.0	1 g/L	12 h	200 rpm	29.2 %	Wang et al. (2021)
Chemical oxidant modified plant biomass carbon	Pickle wastewater	7.0	0.4 g/L	120 min	200 rpm	24.3 %	Liu et al. (2023)
Activated cow bone powder	Palm oil mill effluent (POME)	10.0	125 g/L	120 min	50 rpm	75.6 %	Adeleke et al. (2017)
NaOH-modified peat soil	Palm oil mill effluent (POME)	7.0	5.7 g/L	39 min	50 rpm	69.1 %	This study

(Ohale et al., 2022). In another study, coconut shell activated carbon modified peat soil adsorbent showed 70 % removal of NH_3-N from MSW landfill leachate within 120 min (Detho et al., 2022). The promising removal of ammoniacal nitrogen (75.6 % within 120 min) from POME was demonstrated by adsorbent prepared from activated cow bone powder (Adeleke et al., 2017). The rapid removal of NH_3-N (69.1 % within 39 min) was achieved by chemically modified peat soil in this study compared to previously reported studies.

4. Conclusions

The naturally abundant peat soil was chemically activated to be utilized as an adsorbent for the removal of NH_3-N from POME. The water-holding capacity, bulk density, porosity, and BET surface area of 1:20 NaOH modified peat soil improved remarkably. The SEM images of modified peat soil showed a more porous space structure with larger voids. The results of FTIR characterization demonstrated representative stretching vibrations of functional groups of C–O, O═C═O, C–H, and O–H on the surface of the peat soil. The removal efficiency of adsorbents was tested on different experimental conditions such as adsorbent dose, agitation rate, and contact time. The experimental parameters were optimized using the central composite design (CCD) of RSM. The results showed that the treatment of POME for removal of NH_3-N was optimum at adsorbent dosage of 5.71 g/L, 50 rpm, and 38.96 min, respectively. The average ammoniacal nitrogen removal rate at optimized conditions of fresh adsorbents was observed 53.2 %, 69.1 % and 61.6 % for raw, 1:20 NaOH and 1:30 NaOH activated peat soils, respectively. The findings revealed considerable improvement of modified peat soil compared to raw peat soil. The interaction between the adsorbent dose and contact time was found significant ($p<0.01$) when peat soil activated using 1:20 NaOH, while the interaction between adsorbent dose and agitation rate showed significant ($p<0.01$) for 1:30 activation ratio. The observed and predicted reduction of NH_3-N were 69.06 vs. 64.06 % at 1:20 activation ratio and 61.57 vs. 58.74 % at 1:30 activation ratio, respectively. The optimized outcomes had a desirability of 0.81, demonstrating the applicability of the proposed models.

CRediT authorship contribution statement

Md. Arif Hossen: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Formal analysis, Data curation, Conceptualization. **Nurashikin Yaacof:** Writing – review & editing, Supervision, Funding acquisition. **Fariha Najwa Azahar:** Writing – original draft, Investigation. **Noraziah Ahmad:** Writing – review & editing, Funding acquisition. **Azrina Abd Aziz:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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